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(71) Applicant *(for all designated States except US)*: C.I.R.S. S.P.A. [IT/IT]; Colafonda - Cavanella Po, I-45010 Rovigo (IT).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: CARLIN, Francesco [IT/IT]; Colafonda - Cavanella Po, I-45010 Rovigo (IT). CARLIN, Paolo [IT/IT]; Colafonda - Cavanella Po, I-45010 Rovigo (IT).

(74) Agent: D'AGOSTINI, Giovanni; D'Agostini Organizzazione, Via G. Giusti, 17, I-33100 Udine (IT).

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(54) Title: METHOD AND PLANT FOR THE PRODUCTION OF POLYVINYLCHLORIDE IN AQUEOUS SUSPENSION WITH RECOVERY OF REFLUXES

(57) Abstract

Method for Polyvinylchloride production in aqueous suspension with recovery of refluxes, that provides for the use of a plant for Polyvinylchloride production that has at least one reactor to transform the vinyl chloride monomer into Polyvinylchloride in aqueous suspension and vinyl chloride monomer wastes into the gaseous state, and to separate at least one part of the water from the aqueous Polyvinylchloride suspension, as reflux water, characterized by the fact that said reflux water is recycled in the reactor(s) in polymerization phase.

DESCRIPTION

METHOD AND PLANT FOR THE PRODUCTION OF POLYVINYLCHLORIDE IN AQUEOUS SUSPENSION WITH RECOVERY OF REFLUXES

Technical Field

This invention has for object a method and plant for the production of Polyvinylchloride in aqueous suspension with reflux recovery.

Background Art

At the present state of the art the production system of Polyvinylchloride in aqueous suspension is already known.

This method consists of polymerizing in a discontinuous way, the vinyl chloride monomer (VCM), dispersed in water, by the use of suspension agents and the use of catalysts of the oleosoluble peroxide type in the VCM itself.

This polymerizing reaction is carried out in reactors of different sizes.

These reactors are in substance containers resistant to pressure and provided with agitators that keep the contents in agitation during reaction and as such in suspension.

The same reactors are provided with cooling or heating jacket for adjusting and/or maintaining the temperature at optimal reaction conditions.

Big size reactors of e.g. 80-130 cubic metres, are similarly provided with a condenser placed on the upper side of the reactor that allows to increase in a considerable way the exchange surface of the reactor itself, increasing in this way its productive capacity, by removal of the large amount of the exothermic reaction heat that is

set free during the polymerizing itself.

The reaction occurs under constant pressure.

At the end of the reaction, a gradual drop in pressure is observed that indicates that the loaded VCM has changed into solid Polyvinylchloride (PVCS) in aqueous suspension in one part, wherefore the aqueous suspension still contains the un-reacted vinyl chloride monomer (VCM).

The percentage of vinyl chloride monomer (VCM) that remains embodied in the aqueous suspension can vary between 8% and 20% in weight of the total amount initially loaded, depending on technologies and load formulations adopted.

The entire suspension is then submitted to a degasing, by opening a gas exit system from the reactor.

This operation completely sets free the aqueous suspension of the vinyl chloride monomer (VCM), because at this temperature (solution still hot), the whole monomer is in the gaseous state.

The aqueous suspension therefore without monomer and with the Polyvinylchloride (PVCS) in suspension in the form of solid particles, is then discharged by the reactor and submitted to filtration or centrifugation to remove the greatest possible amount of water (60-70% in weight of the entire suspension) from the polymer.

The polymer is then sent to a desiccation plant where it is completely dried for marketing.

The drawbacks that result are:

- the necessity to liquify the gaseous monomer coming from the reactor for its complete recovery and reloading in the subsequent reactions with high costs and above all with serious danger of immission into the external atmosphere with highly toxic and

polluting effects.

- the reflux water resulting from the separation of Polyvinylchloride (PVCS), still contains Polyvinylchloride wastes (PVCS) that are also highly pollutant.

If one considers that in order to produce 1 ton of PVCS, approximately 3 tons of water are normally used, one understands the large amount of such environmental pollution, considering that on average about 1000 p.p.m. of PVCS remain in the reflux waters, in micropolymer form not easily separable from the water itself, precisely because the particles in solution are minute in size.

The most obvious thought would be that of re-using the reflux water in a subsequent reaction, but this is not possible because the micropolymers contained in it would generate centers of polymerization that would irreparably damage the quality of the finished product.

Therefore these reflux waters are regularly sent to very expensive industrial depuration plants with further environmental pollution problems for the elimination of separate products.

Even though the waters have been purified, they cannot be re-used in new reloads because even after the depuration processes the necessary degree of purity is not reached.

For the gas one is obliged to use expensive liquefaction and recovery plants for the subsequent re-use.

Furthermore it is known that one can have difficult moments during reactions, necessity of immediate pressure discharge and/or risk and/or danger of explosion.

The aim of the present invention is to eliminate the above-

mentioned drawbacks.

In particular, attention is drawn on the possibility of recovery of reflux waters directly in the reactor and surprisingly it was found that, if the reflux waters are added after the reaction has started and after the microparticles of PVCS have begun their formation (therefore, already structured genetically), there is no damage to the reaction and no qualitative damaging of the product, probably because the microparticles of the reflux waters are no longer the genetic basis of the reaction but particles that will unite with the previous ones already codified and therefore without introducing substantial alterations in them.

In this way the problem of recovery of reflux waters is completely solved, because they are re-used in the continuous process, without ever having discharged on the outside.

As claimed the problem is solved therefore, by the use of a plant for Polyvinylchloride production that has at least one reactor to transform the vinyl chloride monomer into Polyvinylchloride in aqueous suspension and vinyl chloride monomer wastes to the gaseous state, and to separate at least one part of the water from the aqueous Polyvinylchloride suspension, as reflux water, characterized by the fact that the said reflux water is loaded in polymerization reactors, during the polymerization process.

This technique of adding reflux waters does not damage the polymerization process inasmuch as the main chemo-physical and morphologic characteristics of formation of PVCS particles have already been formed in the presence of water and pure VCM monomer.

Advantageously the plant has at least two reactors interconnected with each other to operate in a continuous way.

In this way during a process that could advantageously proceed without continuity, firstly starting one reactor and then the other, staggered from the first,:

- the toxic gases can be recovered, discharging them from one reactor to the other;
- load at the right moment in one reactor and then the other, the reflux waters from the first on the second and vice versa from the second on the first.

The interconnection can be carried out by a third reactor or interconnection container, that acts as a lung for a total continuity of plants.

Advantageously the connection between the two reactors can be made by means of a container or even an intermediate reactor or third reactor that advantageously is smaller for the reasons that will be hereafter explained.

In this way the third reactor or interconnection container, can act as a lung with the reflux gaseous and liquids of the other two, with transfer at the right moment in the process phases, or of possible emergency, from one to the other and this allows the continuity of the process without recovery units.

Advantageously the interconnection container or third reactor can act as a lung for the gaseous and liquid refluxes of one or the other of the two main reactors, with transfer at the right moment in the process phases, or of possible emergency, from one to the other and this allows the continuity of the process without recovery units.

The plant operates in a way that the vinyl chlorinated monomer not reacted in one of the two reactors, after liquefaction, is transferred to the second reactor, already in reaction phase.

Said reflux water is loaded into the main polymerizing reactors, during the polymerizing process.

This technique of reflux water addition does not damage the process of polymerizing inasmuch the main chemical-physical and morphologic characteristics of formation of the PVCS particles have already been formed in presence of pure water and monomer VCM.

Advantageously the two reactors are started preferably staggered from 30 to 70% of the total reaction time.

In this way the degasing phase of a reactor coincides with the central phase of polymerization of the second reactor.

A further advantage results from the fact that in case of serious emergency the interconnection container or third reactor can collect the vinyl chloride monomer condensates, mix them with the inhibitor and supply the operator a precious elongation of handling and decision times before the opening of the safety valves for excess of internal pressure.

Process:

At the beginning of the loading the main reactor is loaded with a smaller amount of water when compared to the traditional formulations, in order to absolutely provide a necessity of further water addition during the process.

Advantageously the lack of water in load will be lower than 40%-70% preferably 60% of the initial load for selfsufficiency.

Having reached the reaction time of 60 minutes (between 5% and 20% of the total reaction time) to the aqueous solution in violent reaction, the water taken away at the beginning of the loading is mising, and such is compensated for by the reflux waters of the PVCS separation.

In the meantime, in the first reactor the conclusive phase of discharge of VMC vapours is reached, that is discharged into the third reactor at the liquid state.

After the addition of the reflux waters, and reaching the central part of polymerization phase, one proceeds to the addition of VCM coming from the other reactor.

Advantageously therefore, after or during the addition of the reflux waters, one proceeds to the addition of the VCM coming from the other reactor, after its reaction has ended.

These and other advantages will appear from the subsequent description of a preferential solution with the help of the included drawings the execution details of which of are not to be considered limitative but only given as an example.

Figure 1 is a schematic view of the plant according to the present invention.

Referring to the figures it is noticed that with 1 and 2 the reactors interconnected from tank 3 are indicated, that may preferably also be a third mini-reactor to polymerize or stop VCM monomer in case of emergency or necessity (for example imminent danger of opening of security valves of main reactors 1 and/or 2.)

With 12-22 the VCM monomer is indicated at the gaseous state in main reactors 1,2.

With 11 and 21 the PVCS aqueous suspension is indicated together with VMC liquid monomer in main reactors 1,2.

With 4 and 5 the head capacitors of reactors 1 and 2 are indicated.

With 6 the reflux water loading lines of PVCS separation are indicated.

With 7 the unloading of PVCS in aqueous suspension from the reactors is indicated.

With 8 the filtration device for separation of PVCS from the water and the recircling of the water to reactors 1 and 2 is indicated, according to the described and claimed method, or after a certain period of time from the respective reaction starting phases.

Obviously filtration system 8 will operate alternatively from one on to the other of the two reactors 1,2, in such a way that, in the continuous cycle, when a reactor has completed its polymerization, and the PVCS product + water has been unloaded and filtered, etc., the reflux water is loaded on the other that is already in an advanced reaction phase, and vice versa.

CLAIMS

1. Method for Polyvinylchloride production in aqueous suspension with recovery of refluxes, that provides for the use of a plant for Polyvinylchloride production that has at least one reactor to transform the vinyl chloride monomer into Polyvinylchloride in aqueous suspension and vinyl chloride monomer wastes into the gaseous state, and to separate at least one part of the water from the aqueous Polyvinylchloride suspension, as reflux water, characterized by the fact that said reflux water is recycled in the reactor/s in polymerization phase.

2. A plant for the polyvinylchloride production, using a method according to claim 1., of the type in which it uses at least one reactor to transform the vinyl chloride monomer into polyvinylchloride in aqueous suspension and vinyl chloride monomer wastes into the gaseous state, and separate at least one part of the water from the aqueous polyvinylchloride suspension, as reflux water, characterized by the fact that this plant includes at least two reactors (1, 2) interconnected one with the other (3).

3. Method as claimed in claim 1., using a plant according claim 2. characterized by the fact that said reflux water is loaded into the main polymerizing reactors, during the polymerizing process.

4. Method according to preceding claims, characterized by the fact that while a reactor is still, its reflux waters (8) is loaded into the other one that is in reaction phase.

5. Method according to preceding claims, characterized by the fact that the plant operates in order that un-reacted vinyl chloride monomer in one of the two reactors (1 or 2), after liquefaction, is transferred (3) to the second reactor (2 or 1), this already being in reaction phase.

6. Method according to preceding claims, using a plant according to claim 2, characterized by the fact that the two reactors are started at times staggered one from the other.

7. Method according to preceding claims, using a plant according to claim 2, characterized by the fact that the two reactors are started at times staggered one from the other, of a time comprised between 30 and 70% of total reaction time.

8. Method according to preceding claims, using a plant according to claim 2, characterized by the fact that at the beginning of loading, the main reactor is loaded with a smaller amount of water when compared to the traditional formulations, in order to absolutely provide a necessity of further water addition during process.

9. Method according to claim 1, using a plant according to claim 2, characterized by the fact that the lack of water in load is lower than 40%-70% preferably 60% of the initial load for selfsufficiency.

10. Method according to claim 1, characterized by the fact that when reaction time comprised between 5% and 20% of total reaction time is reached, the missing water is supplied by means of reflux waters obtained by PVCS separation process.

11. Method according to claim 1, using a plant according to claim 2, characterized by the fact that after or during the addition of reflux waters, one proceeds to VMC addition coming from the other reactor, after the end of its reaction.

12. Plant according to previous claims, characterized by the fact that it has an intermediate lung container (3) as interconnection element between the two said reactors (1,2).

13. Plant according to preceding claims, characterized by the fact that it has an intermediate lung reactor (3), as interconnection element

between the two said reactors (1,2) and of the same type.

14. Plant according to preceding claims, characterized by the fact that it has an intermediate container or intermediate lung reactor (3), as interconnection element between the two said reactors (1,2) that connects the upper peaks of the same for parking and subsequent transfer at the right moment the respective gases developed from one reactor to another (12,22), after at least partial condensation (4,5).

15. Plant according to preceding claims, characterized by the fact that the said interconnection element between the two said reactors (1,2), also includes a separating recircling device of Polyvinylchloride in aqueous suspension and water (8), in order to recirculate it from one on to the other of the two main reactors (1,2).

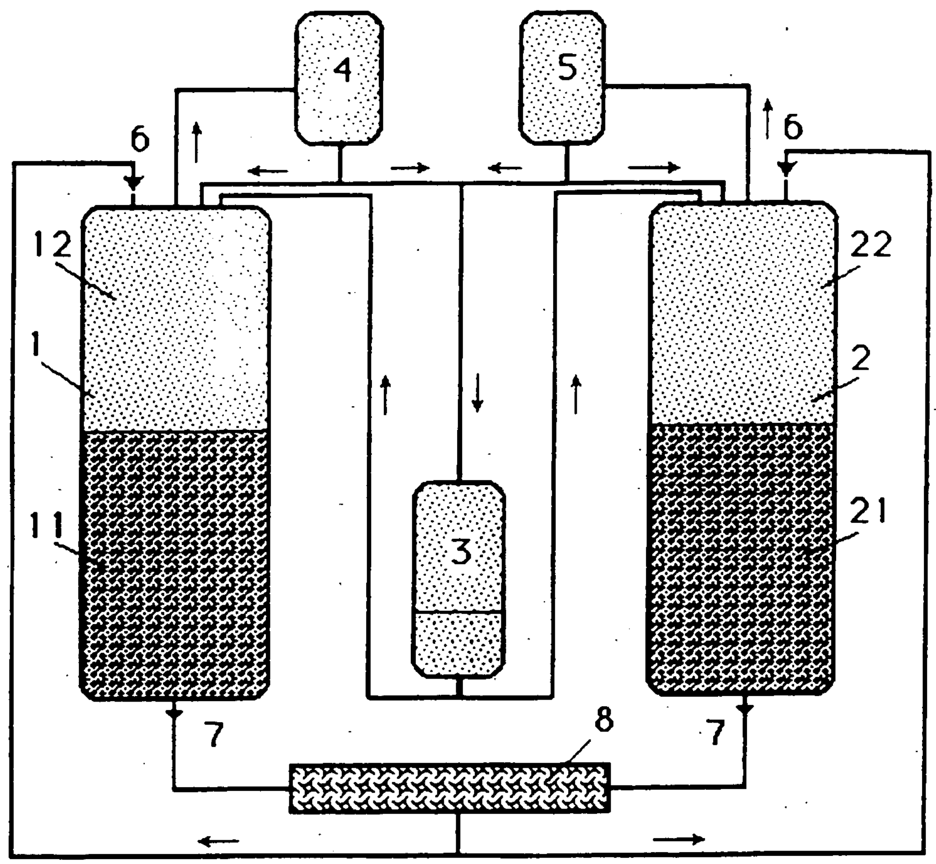

FIG.1

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IT 95/00209

A. CLASSIFICATION OF SUBJECT MATTER

C 08 F 6/24,114/06

According to International Patent Classification (IPC) or to both national classification and IPC 6

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C 08 F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☐ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
11 March 1996	03. 04. 96

Name and mailing address of the ISA	Authorized officer
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ANHANG

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

ANNEX

to the International Search Report to the International Patent Application No.

ANNEXE

au rapport de recherche international relatif à la demande de brevet international n°

PCT/IT 95/00209 SAE 122652

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.

La presénte annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les reseignements fournis sont donnés à titre indicatif et n'engagent pas la responsibilité de l'Office.

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